

**NON EQUILIBRIUM SYNTHESIS OF IMPROVED
SURFACE PROPERTIES BY ION BEAM ASSISTED
DEPOSITION**

FINAL TECHNICAL REPORT

Grant No. DAAH04-96-1-0127

SUBMITTED

10 October 2000

STARTUP DATE AND DURATION: 1 April 96 to 31 March 99

PRINCIPAL INVESTIGATOR: Prof. Robert L. Zimmerman
Center for Irradiation of Materials
Alabama A&M University
P.O. Box 1447
Normal, AL 35762-1447
(256) 851-5866
rlzimm@cim.aamu.edu

DATE: 23 October 2000

20001122 141

REPORT DOCUMENTATION PAGE

Form Approved
OMB NO. 0704-0188

Public Reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comment regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188,) Washington, DC 20503.

1. AGENCY USE ONLY (Leave Blank)	2. REPORT DATE 23 October 2000	3. REPORT TYPE AND DATES COVERED Final Report	
4. TITLE AND SUBTITLE Non Equilibrium Synthesis of Improved Surface Properties by Ion Beam Assisted Deposition		5. FUNDING NUMBERS DAAH04-96-1-0127	
6. AUTHOR(S) Robert L. Zimmerman			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Alabama A&M University Normal, AL 35762-1447		8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) U. S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211		10. SPONSORING / MONITORING AGENCY REPORT NUMBER ARO 35669.1-MS-SAH	
11. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.			
12 a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited.		12 b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) We have acquired a facility combining ion beam bombardment with physical vapor deposition (IBAD) to increase the resistance to wear, fatigue, corrosion and oxidation of material surfaces important to the Department of Defense. The IBAD facility supplements the MeV and keV implantation capabilities at the Center for Irradiation of Materials at Alabama A&M University. The vacuum chamber and pumps, a 12-cm ion gun and a 10-inch Cryopump and an ion source upgrade were installed the first year and made possible the production of IBAD coatings the first year. In the second year, we acquired one 15-kilowatt and two 6-kilowatt electron guns, making our IBAD facility one of the most powerful and			
14. SUBJECT TERMS		15. NUMBER OF PAGES	
		16. PRICE CODE	
17. SECURITY CLASSIFICATION OR REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION ON THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL

REPORT DOCUMENTATION PAGE (SF298)
(Continuation Sheet)

resourceful in the country. We have produced IBAD coatings of refractory materials such as Al_2O_3 , SiC , Si_2O_3 , WC , and Ni_2Si as well as many metal films. In the third year, we purchased a Raman spectrometer to characterize the surfaces produced, especially diamond like carbon and modified glassy polymeric carbon.

Funds allocated to this project allow AAMU to continue the involvement of minority graduate and undergraduate students in research at the frontier of materials science. One minority student obtained his Ph. D. and numerous other minority students obtained their support from this project.

TABLE OF CONTENTS

TABLE OF CONTENTS.....	2
Abstract.....	3
1. Introduction.....	4
1.1 Technical Overview.....	4
Figure 1	5
Figure 2	6
1.2 Technical Approach.....	6
Figures 3-4	7
1.3 Relevance to the Department of Defense Mission	8
1.4 Relevance to AAMU.....	8
2. Progress of the Project.....	8
2.1 Equipment Acquisition	8
2.2 Accomplishments.....	9
Figures 5-6	10
Figures 7-8	12
Figures 9-13	13
2.3 Educational Component	14
References	15

ABSTRACT

We have acquired and installed a hybrid combination of ion beam bombardment in conjunction with physical vapor deposition to modify surface sensitive properties of critical military materials. The energy transfer from Ion Beam Assisted Deposition (IBAD) permits nonequilibrium processes at the surface that are impossible by chemical means and do not have the negative environmental consequences of the traditional wet processes. The objective is to obtain enhanced properties important to the Department of Defense that include increase in wear, fatigue, corrosion and oxidation resistance. We have used the MeV and keV implantation capabilities at the Center for Irradiation of Materials (CIM) at Alabama A&M University (AAMU) and have dedicated a beam line for this work. We have used inert, as well as chemically active, energetic ions together with vapor deposition to synthesize novel superhard films and we have studied the improved surface properties of these films and interface layers.

The vacuum chamber and pumps and an ion source upgrade were installed the first year and made possible the production of IBAD coatings with the AAMU Pelletron and other facilities that were present at the time. During the first year, we also removed the 8-cm ion gun and the 8-inch Crypump and modified our facility to accommodate a 12-cm ion gun and a 10-inch Crypump that anticipates future high power ion beam assisted operations.

In the second year, we acquired two 6-kilowatt and one 15-kilowatt electron guns, making our IBAD facility one of the most powerful and resourceful in the country. With it we have produced IBAD coatings of refractory materials such as Al_2O_3 , SiC , Si_2O_3 , WC , and Ni_2Si as well as many metal films. With the high fluence ion source and these electron gun evaporators, the IBAD coating technique may be scaled up to study the feasibility and cost effectiveness of practical applications in accordance with the results obtained from fundamental research results already in hand.

In the third year, we purchased a Raman spectrometer to replace the outside services that we had been using to characterize some aspects of the surfaces produced, especially diamond like carbon and modified glassy polymeric carbon. This acquisition was proposed in collaboration with researchers at Oak Ridge National Laboratory.

Funds allocated to this project allow CIM to continue the involvement of minority graduate and undergraduate students in research at the frontier of materials science. During the period of this report, one minority graduate obtained his Ph. D. and numerous other minority students obtained their scientific initiation participating in the the acquisition and testing of the equipment and first operations of this facility. The references at the end of this report may be used as a basis for judging the scientific production and involvement of students the resulted because of the support for this project.

1. INTRODUCTION

The Ion Beam Assisted Deposition Laboratory (IBAD) at the Center for Irradiation of Materials at Alabama A&M University has undergone major development with the acquisition of the IBAD chamber and supporting equipment (Figs 1 and 2). This equipment was funded by the **Department of Defense (DoD)/U.S. Army, Grant No. DAAG55-97-1-0060**. ("Advanced Instrumentation for Nonequilibrium Processing," reported January 1999). Other equipment and accessories for the IBAD laboratory were acquired with an **ARO/AFOSR Grant No. F49620-98-1-0497** and has been reported elsewhere. The objectives of the research undertaken with the IBAD and associated equipment have been to obtain enhanced properties important to the DoD that included increase wear, fatigue, corrosion and oxidation.

The staff and students at CIM have been actively collaborating with other research institutions both nationally and internationally. These include almost all of the universities, NASA and the US Army laboratories in Alabama and many institutions outside Alabama. The Oak Ridge National Laboratory in Tennessee and the Army Research Laboratory at Aberdeen, Maryland, periodically accept CIM researchers as users of research equipment on a basis equal to their professional staff. Outside the United States there are the Claude Bernard University, Lyon, France, the Max Planck Institute, Heidelberg, Germany and the University of São Paulo, Brazil. These three institutions have an especially close relationship with CIM, exchanging staff and students, collaborating with research of mutual interest, and publishing jointly.

1.1 Technical Overview

Films on the surfaces of solid materials have long been employed to give the coated material improved or new properties. Wear and corrosion resistance and reduced friction as well as new optical, magnetic and electrical properties may be obtained. Coatings have traditionally been made chemically from solution or by vapor deposition in a vacuum or in a reactive gas atmosphere.

With the development of ion accelerators, ion beam deposition has produced films with precise control of the interface with the substrate independently of its chemical affinity with the imbedded ions. Physical vapor deposition or chemical vapor deposition has been accomplished during simultaneous ion beam bombardment only relatively recently [1,2]. Figure 1 shows the concept of Ion Beam Assisted Deposition (IBAD). Low energy atoms of coating material are transferred to the target by evaporation from an appropriate source. Simultaneously, high energy ions transfer energy to the coating and target which may be maintained at a low temperature. The energy transfer permits nonequilibrium processes to occur in the growing film that are independent of chemical affinities of the materials. It is this energy transfer that gives the coating desirable properties. IBAD allows the production of modified surfaces thicker than possible with direct ion implantation or ion beam deposition and the films often have improved optical properties, higher density and hardness, superior abrasion resistance and adhesion compared with those produced by simple vapor deposition. Because multilayer films and patterns are possible, the protective coatings may serve also as sensors, antennas, and infrared or radar absorbers. There is no process waste or other environmentally adverse factors as with electroplating.

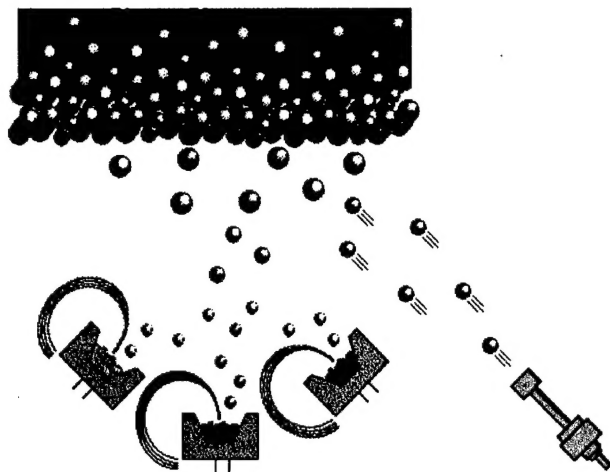


Figure 1: Schematic of the AAMU IBAD facility. A broad beam 10 cm ion gun supplies ions of selective gases with energies to 2 keV. The three e-beam evaporators can be operated simultaneously or sequentially to deposit films under nonequilibrium conditions on materials on a target held at temperatures up to 1000°C.

Conventional corrosion resistant coatings on incompatible materials suffer from poor adhesion and localized defects, such as pores, which cause delamination and localized corrosion. Ion implantation can often overcome the problems associated with adhesion and porosity and is also capable of producing unique surface alloys, including amorphous surface alloys, unattainable by any other ambient temperature alloying technique. Implantation by itself, however, is restricted for many commercial applications because of the limited layer thickness that it can produce. IBAD processing surmounts some of these limitations by achieving both excellent adhesion and arbitrary thickness. Figure 2 is a photograph of the AAMU IBAD laboratory at the Alabama A&M University. Unique films and layers may be produced by sequential or simultaneous deposition from combinations of three high power electron guns, and the broad beam ion gun.

Usually the IBAD experimental parameters are varied to optimize a single characteristic of the deposited film that is most important in a particular application. In fortunate cases more desirable characteristics are obtained. For example, Fountzoulas *et al.* [3] have shown that diamond like carbon (DLC) films deposited on Silicon during ion bombardment retain their hardness and low coefficient of friction even in humid atmospheres where conventional DLC films exhibit an order magnitude more friction. Franzen *et al.* have made IBAD films of aluminum oxide with improved density, hardness and index of refraction [4].

We proposed to use the Alabama A&M University Pelletron ion accelerator and the IBAD facility to investigate the feasibility of producing films with hardness and tribological properties tailored to enhance specific characteristics of military importance. Diamond like carbon (DLC) films, produced at the ARL-WMRD facilities at Aberdeen, Maryland, were the first to be characterized by the AAMU hydrogen profiling facility. An example of the results is presented in this report. With the completion of the AAMU IBAD facility in mid 1998, films of sapphire (Al_2O_3), SiC, Ni_2Si and many metals have been produced and characterized. Figure 3 is an interferogram of a sapphire film that was deposited on glass with the IBAD process at AAMU. Because the index of refraction of sapphire is larger than that of glass, the sapphire film is an optical wave guide. We have used its waveguide properties to infer the excellent crystallinity of the IBAD sapphire film. Ongoing research involves Al_2O_3 , Ni_2Si , WC and other hard materials.



Figure 2: Photograph of the IBAD laboratory. The 3 e-beam evaporators and ion beam gun are mounted on flanges on the floor plate of the 36-inch vacuum chamber. The upper 24 inches of the chamber can be lifted to expose the e-gun crucibles and the rotating temperature controlled target holder. Two 6-kw e-beam power supplies and scanning controls are in the rack at the right. The single 15-kw e-beam supply is visible behind the rack. Three gas supplies are available from the blue panel and a fourth gas can be supplied from the cylinder on the left. The sloping panel at left is the ion beam controls and the white panel is the vacuum and chamber lift controls. A 10-inch Cryopump and its compressor are obscured under and behind the chamber.

1.2 Technical Approach

In this project, we used keV and MeV implantation to produce inert, as well as chemically active, ions to activate chemical and diffusion processes on surfaces at ordinary temperatures. This avoids the high temperatures normally required for producing tribological coatings such as Al_2O_3 , SiC , Ni_2Si , TiN , TiC [5,6,7] or diamond like carbon (DLC) [3]. The effects of these energetic ions promote the adhesion of the concurrently vapor deposited film, densify the films, and help to chemically incorporate reactive ions into the coatings.

The significant parameters for IBAD are a) the ratio of the fluence of atoms used to grow the film to that of the bombarding ions, b) the energy and type of bombarding ion, and c) substrate parameters, such as temperature and electric field bias. We have acquired and installed a new high current ion source that delivers intense ion beams of specific isotopes of virtually every element in the periodic table.

The first films studied were DLC made in collaboration with researchers at ARL-WMRD from a precursor vapor of pentaphenyl-trimethyl-trisiloxane (a Dow Corning silicone oil). The vapor pressure of this precursor is easily controlled by heating a reservoir of the liquid in the experimental chamber. Substrates immersed in the vapor of the precursor are bombarded by ions of known species, energy and fluence. Although DLC films have recently been produced by this technique, the fundamental processes involved have not yet been clearly established nor optimized. We have used the AAMU hydrogen profiling facility to study the hydrogen content of these DLC films. These profiles are shown later (Fig. 7) in this report. Other techniques at ARL-WMRD were used to measure the microhardness of the DLC films as a function of dose

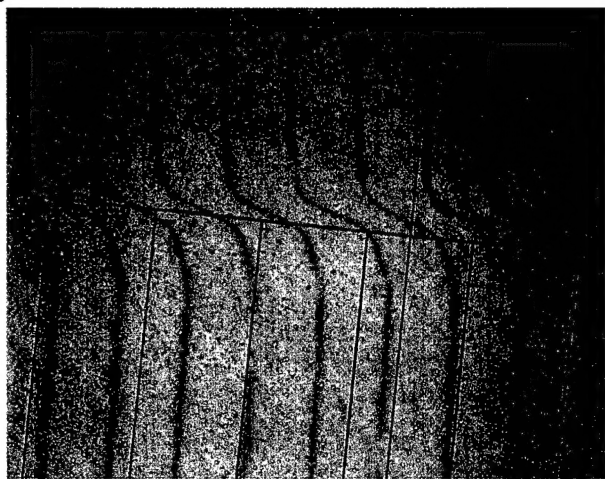


Figure 3: Sapphire (Al_2O_3) film produced by IBAD that has been overlaid with a gold film to permit an interferometric measurement of the film thickness.

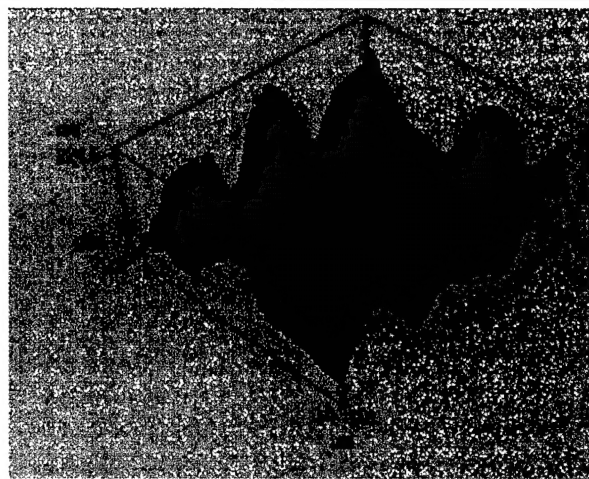


Figure 4: Interferometrically revealed profile of aluminum film produced by e-beam evaporation through a 1000 mesh (the unit square is 25 μmeters on a side). The bumps are approximately 350 nm from base to peak.

and energy per bombarding ion. The chemical state at the interface between the processed film and the substrate were studied with ESCA as well as SIMS. The tribological properties of the films in realistic environments were studied by standard techniques.

Other films, such as Al_2O_3 , SiC and Ni_2Si were produced and characterized at the AAMU IBAD experimental program. These hard coatings, as well as many types of metal films (See Fig. 4), were applied to low temperature substrates, such as polymers, as well as to metals at near ambient temperatures. Polycarbonate instrument and vehicle windows, as well as the new glassy polymeric carbon, are of interest to DoD. Often these hard coatings exhibit low friction in contact with materials with the same or another coating even in harsh environments.

The Howard J. Foster Center for Irradiation of Material at the Alabama A&M University has accumulated significant experience in ion beam analysis techniques [10-24]. Innovative methods have been developed to detect impurities in light elements [8], notably in glassy polymeric carbon [9,10,11], a material whose development has been pioneered by researchers at AAMU, and in stainless steel alloys [12]. The detection methods include nuclear detection techniques, such as Rutherford Backscattering Spectrometry (RBS), Nuclear Reaction Analysis (NRA) and Elastic Recoil Detection (ERD), as well as other surface specific analytical techniques. Many of these techniques are unique in allowing analysis of elemental content and crystalline states as a function of depth near the surface of solids and are often the only techniques that allow accurate measurements of those properties of hard coatings as well as in producing modifications of the properties of optical [16-19,21,22], polymeric [16,20] and materials for sensors [24] and medical [23] applications by ion bombardment. Adjacent laboratories at AAMU contain all the equipment necessary to accomplish conventional engineering analysis, such as hardness, tensile strength and thermal properties and to accomplish infrared optical spectroscopy. Raman spectroscopic measurements of these coatings are desirable, and the acquisition and installation of a micro Raman facility has been accomplished in the period reported here. Raman measurements are now a routine part of the characterization of films produced with the IBAD facility.

The Center for Irradiation of Materials also has experience in modifying materials by ion bombardment. Most significant for the understanding of materials produced or modified with the IBAD facility are the modifications made near the surface of glassy polymeric carbon [13] and its precursor resin, phenolformaldehyde [9-11,14,15].

1.3 Relevance to the Department of Defense Mission

Plasma processing as well as IBAD are the two topics in which the U.S. Army has invested for the last few years to substitute the electrochemical wet techniques. Our effort promises to develop innovative processes to produce better protective surfaces with more environmentally friendly coating and techniques. Candidate applications include replacement for hard Cr electroplate wear resistant coating used extensively in the aerospace industry. Given the current concern for environmentally benign processes, there is interest and considerable investment in finding alternatives. A more complete understanding of the fundamental processes involved in IBAD is a primary objective of our research. Once these fundamental processes are understood, specifically designed ion sources and accelerators that are already being developed will make the IBAD process more cost competitive.

The development of the IBAD process has resulted in a number of DoD applications, ranging from robust optical coatings to surface protective coatings for wear, corrosion and fatigue improvement. Recent DoD thrusts include environmental programs exploring these benign, dry ion beam techniques for supplanting the wet electroplating processes for Cr and Cd, processes that are under increasing scrutiny at DoD installations. We have coordinated our work with Army researchers already working on IBAD coatings at the Materials Directorate of the Army Research Laboratory [3].

1.4 Relevance to AAMU

Alabama A&M University, an Historically Black College and University (HBCU), has sought and has achieved an increasingly important role in involving faculty and students in research of interest to the Department of Defense (DoD). This project continues the collaboration of AAMU researchers and students directly with the Army Research Development Centers (RDECs). Graduate students and exceptionally well qualified undergraduate students have the opportunity to involve themselves with research techniques of proven value for coating of materials of interest to the DoD together with students and staff from other US and foreign universities.

2. Status of the Project

2.1 Equipment Acquisition

We acquired a large vacuum chamber, an ion source and three electron gun vapor sources that constitute our Ion Beam Assisted Deposition (IBAD) system. This equipment was funded by **this project** and by the **DURIP Grant No. DAAG55-97-1-0060**. The IBAD system includes an ion source and three electron gun evaporators strategically deployed in a vacuum chamber large enough to accommodate experimental samples on a 30-inch rotatable stage. Power supplies, vacuum pumps and sensors have been installed and tested (see Figure 2).

A LABRAM fast analytical Raman spectroscopy system has been purchased from Instruments S.A. in Edison, N.J., under **this project** and grant **number ARO/AFOSR Grant No. F49620-98-1-0497**. This system was delivered in January 1999 and immediately entered routine operation. It is used to characterize important aspects of the IBAD grown films. It consists of a basic system, configured with a confocal microprobe for maximum depth and lateral spatial resolution. The standard configuration includes a macro lens, which provides ultimate spectral results in cases of transparent solid and liquid samples. The SMA connector for the interchangeable fiber optical entrance makes the use of the SUPER HEAD fiber probes easy and convenient. Two interchangeable gratings provide both high resolution spectra and a faster overview function for wider wavelength ranges in one system. An appropriate Holographic Notch Filter is incorporated into the system to enable acquisition of Raman spectra with conditions optimized for sensitivity and low frequency performance.

2.2 Accomplishments

In the second year of this project, we implanted keV Cr, Ti, and Si ions as well as MeV V, Au, Ag, and Cu ions at both room temperature and at elevated temperatures into single-crystal c-axis sapphire in order to induce surface compressive stresses and change (increase) the shatter resistance of the surface of the crystal. We used Rutherford Backscattering Spectrometry (RBS) and ion beam channeling to assess the composition and crystallinity of the implanted surfaces. The optical transmittance of the implanted sapphire crystals was examined using both visible spectrum transmission and Fourier Transform Infrared Spectroscopy to ensure that the material remained suitable for application as an optically transparent window.

We are also investigating the effects of energetic ions on the surface roughness of sapphire crystals using photon tunneling and atomic force microscopy. Presently we are using nano-indentation techniques to study the effects of the ion implantation at both room temperature and at elevated temperatures before and after post annealing.

Mr. Michael Dentey, a Ph.D. student from AAMU, worked at ARL-WMRD under the supervision of Dr. D. Demaree and Dr. J. Hirvonen, from the week of June 27 through August 23, 1997, helping with ion beam equipment installation following the lab relocation to Maryland. Because the ARL-WMRD in-house IBAD equipment was not available during the summer of 1997 (it was undergoing refurbishment in Massachusetts), Mr. Dentey assisted other researchers in assembling a nuclear reaction analysis system which is important in the evaluation of IBAD coatings.

Prof. R.L. Zimmerman, the P. I. of this project, worked with Drs. Jim Hirvonen and Derek Demaree at ARL-WMRD for a week during the summer of 1997, helping them optimize the detector electronics of the nuclear reaction analysis system (See Figs. 5,6 and 7) developed at AAMU and recently installed at ARL-WMRD. This work, and the detector design itself, resulted in the coauthorship of publication [25,26] and a paper presented in Proceedings of the 5th Annual U. S. ARL/USMA Technical Symposium, USMA, West Point, NY, 1997, p. 239:

Hydrogen Detection in Metals Using a Coincidence Detector Configuration to Perform Nuclear Reaction Analysis. D. K. Marble, L. Smith, U. S. Military Academy; J. D. Demaree, J. K. Hirvonen, ARL-WMRD; R. Zimmerman, M. Dentey, AAMU.

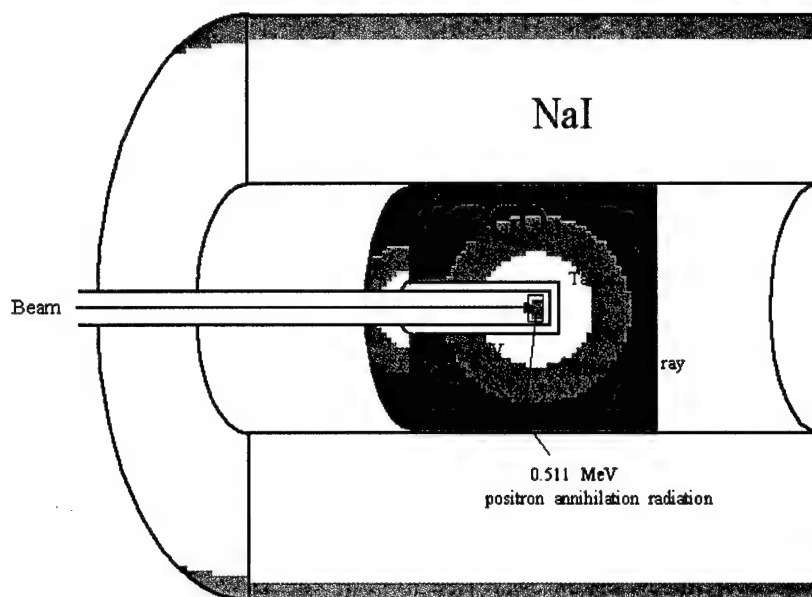


Figure 5: The detector array developed at AAMU and dedicated to depth profiling hydrogen content in IBAD films and other solid materials. The hydrogen concentration in a target is proportional to the number of 4.44 MeV gamma rays produced by the nuclear reaction $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ when the target is bombarded with a ^{15}N ion beam. Background is rejected by a coincidence scheme such that a few ppm hydrogen may be detected.



Figure 6: Photographs of the AAMU detector of trace hydrogen in solid materials. An innovative scheme of detecting simultaneous events from the $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ resonant nuclear reaction in a central Bismuth Germanate scintillator and an outer annular Sodium Iodide scintillator allows the quantitative determination of hydrogen concentration with no external shielding. The instrument was funded with (DoD)/U.S. Army Grant No DAAG55-97-1-0060. A duplicate of this prototype was constructed and is operating at the US Army Research Laboratories (ARL-WMRD) at Aberdeen Proving Grounds, Maryland.

A report on surface modification of optical materials was presented at the Spring MRS meeting which was held in San Francisco, California from April 13-17, 1998 and subsequently published [19,22]:

Mechanical Behavior of Optical Materials Bombarded by High Dose of Various Ions. J. D. Demaree, J. D. Kleinmeyer, U.S. Army Research Laboratory, APG, MD; D. Ila, Center for Irradiation of Materials, Alabama A&M University, Normal AL; D. B. Poker, D. K. Hensley, Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN.

The project being reported was used as a platform to launch a proposal to the **Department of Defense's University Research Instrumentation Program (DURIP)** to fund the IBAD equipment needed in this project and a resulting **Award No. DAAG55-97-1-0060**. The final report of the instrumentation acquired with the DURIP award for the interval, April 1996-March 1998, has been submitted separately.

Prof. R. L. Zimmerman, the P. I. of this project, again worked with Drs. James Hirvonen and Derek Demaree at ARL-WMRD for a week during the summer of 1998, assisting with the installation and testing of a hydrogen detection system, that is used in analysis of the IBAD grown coatings. During the summer of 1998, Abdalla Elsamadicy, a graduate student from Alabama A&M University, assisted with the development of the Hydrogen detection system. Other collaborators on the project included P. Buckley and G. Krasko (ARL), D. K. Marble (USMA-TSU), P. Searson and E. Schwarz (JHU). The detector was designed and built by Prof. Robert Zimmerman at CIM-AAMU. It utilizes a coincidence array consisting of a BGO scintillator surrounded by an annular NaI scintillator specifically for detection of the 4.44 MeV gamma rays from the excited state of ^{12}C following the $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ resonant nuclear reaction used for hydrogen detection in solids. Figure 6 shows the configuration of the fully assembled hydrogen detection system at ARL-WMRD, virtually identical to the prototype funded by ARO, designed and assembled at AAMU described in this technical report.

ARL-WMRD has applied the hydrogen detection system to:

- Hydrogen behavior in high strength steels.
- Erosion behavior of gun barrel alloys & coatings.
- Polymer segregation for adhesives, functional polymers.
- Hydrogen in IBAD & other PVD coatings.

Results of the hydrogen profiling in IBAD grown Si-DLC diamond-like carbon coating were measured using the $^1\text{H}(^{19}\text{F}, \alpha\gamma)^{16}\text{O}$ and $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ reactions. The results for the latter reaction are shown in Fig. 7.

Epi-polished crystals of Al_2O_3 , implanted with various ions at Oak Ridge National Laboratory, were used in a channeling study after post implantation annealing. The RBS channeling spectra are shown in Figures 8 and 9.

Optical absorption measurements were done on the various ion implanted Al_2O_3 samples. The results are shown in Figures 10-13. These optical measurements were performed on the samples that ARL-WMRD used for mechanical testing, the results of which were reported on during the spring 1998 MRS meeting in San Francisco, CA. On March 9, 1998 Dr. Grahm K. Hubler, of the Surface Modification Branch, Condensed Matter and Radiation Sciences Division of the Naval Research Laboratory (NRL) in Washington, D.C., visited CIM. He discussed the

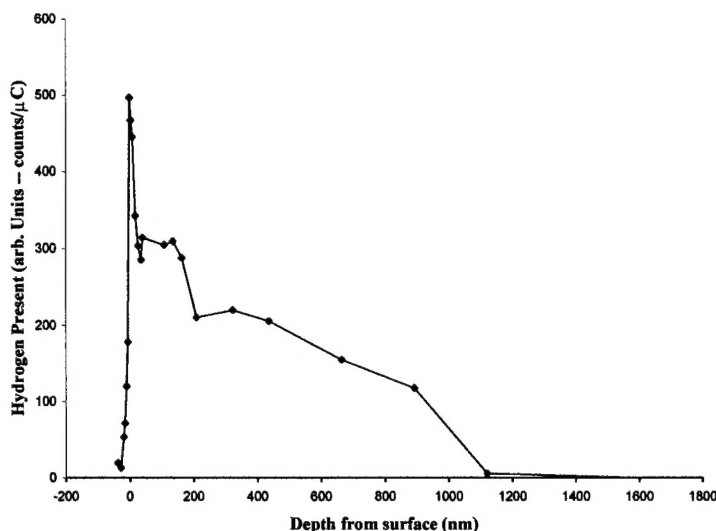


Figure 7: Hydrogen profile in 1 μm thick Si-DLC diamond-like carbon coating using the $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ reaction and the AAMU hydrogen profiling facility shown in Figures 5 and 6.

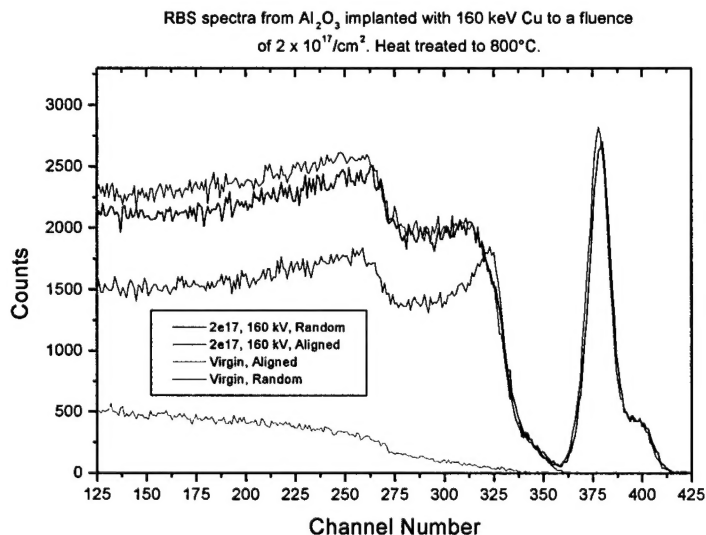


Figure 8: RBS spectra from Al_2O_3 implanted with Cu ions. The depth and distribution of copper in sapphire are obtained from measurements such as these.

IBAD research, thin film processing and laser processing of materials with the research faculty at AAMU and made recommendations on how to increase performance and improve the IBAD system. His recommendation lead to an update of the IBAD Cryopump from the original Cryoplex 8 to the Cryoplex 10, funded by AAMU's matching. As a result of Dr. Hubler's visit, CIM received a contract from NRL for work using the hydrogen detection system that was funded by ARO.

The surface research using the AAMU IBAD facility during 1999 and 2000 resulted in a number of publications and conference reports [19-26] at the International Conferences in Jena, Germany, in Amsterdam, The Netherlands and others. Peer reviewed contributions were accepted for publication together with collaborators at Oak Ridge National Laboratory, the Max Planck Institute, Heidelberg, the University of Sao Paulo and the NASA George Marshall Space Center in Huntsville:

D. Ila, R. L. Zimmerman, E. K. Williams, C. C. Smith, S. Sarkisov, D. B. Poker and D. K. Hensley, "Ion Beam Induced Change in the Optical Properties of Photorefractive Materials, Ion Beam Modification of Materials, Amsterdam, 31-5 September 1998

A. L. Evelyn, Marcello R. Goncalves, D. Ila and R. L. Zimmerman, "Radiation Enhanced Increased Porosity and Roughness of Biomaterials," **Radiation Effects on Insulators**, Jena, 18-21 July 1999.

A. L. Evelyn, D. Ila, R. L. Zimmerman, K. Bhat, D. B. Poker, D. K. Hensley, C. Klatt, S. Kalbitzer, N. Just and C. Drevet, "Ion Beam Modification of PES, PS and PVC Polymers"
 Ion Beam Modification of Materials, Amsterdam, 31-5 September 1998

Nuclear Instruments and Methods in Physics Research B148, 1141-1145 (1999)

R. L. Zimmerman, D. Ila, E. K. Williams, B. Gasic, A. Elsamadicy, A. L. Evelyn, D. B. Poker, D. K. Hensley and David J. Larkin, "Gold, Silver and Copper Nanocrystal Formation in SiC by MeV

Implantation," **Nuclear Instruments and Methods B** 166-167 (2000) 892-896 **18-21 July 1999.**

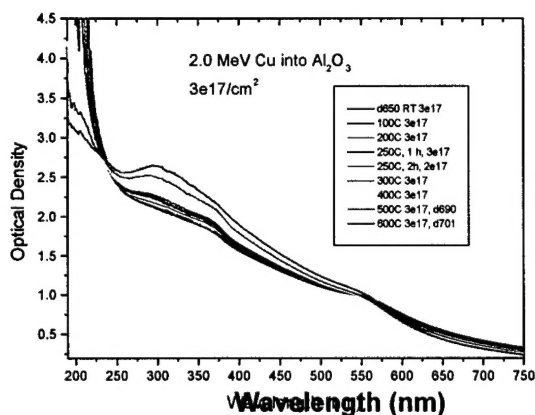


Figure 9: Al₂O₃ implanted with copper

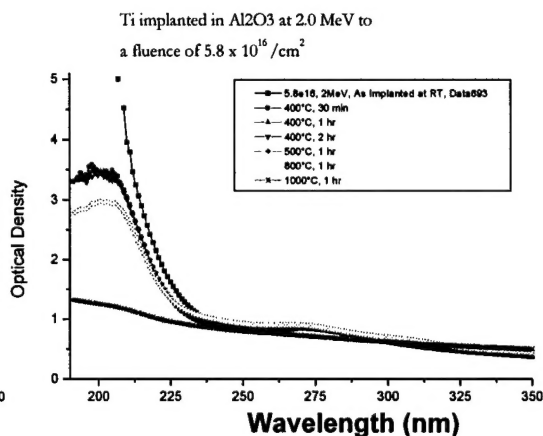


Figure 10: Al₂O₃ implanted with titanium

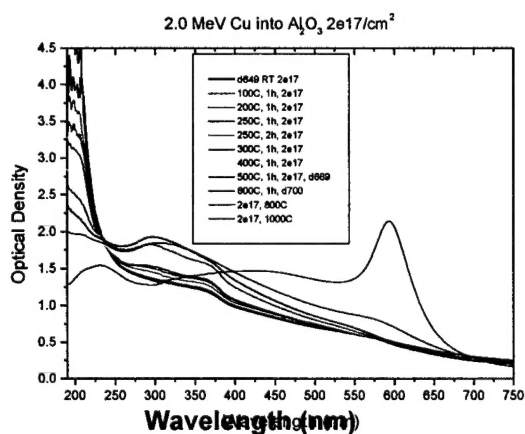


Figure 11: Al₂O₃ implanted with 2 MeV gold and heat treated until nanoclusters form and cause optical absorption at 580 nm.

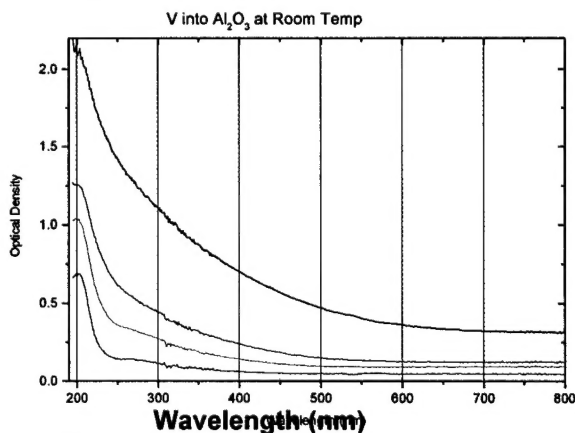


Figure 12: Al₂O₃ implanted with Vanadium

Optical Absorption spectra for 1.5 MeV Ag
 into Al₂O₃ to a Fluence of $8 \times 10^{16}/\text{cm}^2$

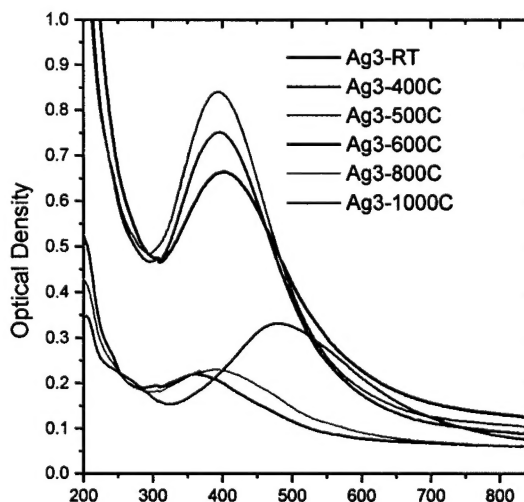


Figure 13: Al₂O₃ implanted with 8×10^{16} silver ions/cm² and heat treated to form silver nanoclusters.

3 Educational Component

Research and education are being integrated under the research grant awarded by DoD. Many students have been and are currently being trained at CIM:

Tracy Battle
Michael Dentey
Jonathan H. Fisher, Ph.D.
Phoebe Huang (Hwei-Ping)
Adrienne Jackson
Branislav Gasic
Patrick Grayson
Kamyar Madani
Claudiu Muntele, Ph. D. (2003)
Nino Mason
LaToshia Miller
Jesse Morris
Rajesh Pandey, UAB-AAMU
Kambiz Arjmand Pyvand
Ying Qian
Marcello Rodriques
Karen Rogers
Abdalla Elsamadicy, Ph. D. (2004)
Daphne Sandfeur
Seif Selemani
Samuel Shorter
Cydale Smith, Ph. D. (2001)
Melvin U. Spurlock
Deon Williams, M. Sc.
Milan Woodard
Zhiqiang "John" Wu

Remi de Bettignes
Christine Borel
Gaetan L. D'Ardhuy
Cecile Drevet
Luc Favre
Christophe Nicod
Nathalie Just
Laetitia R. Barbosa
Koji Takada
Lester Lee Byrd
Wendy J. Booker
Angela Davis
Sharon Davis
David Shaen Hood
Hazelina J. Jackson
Shenell Y. Miller
Latasha C. Raven
NaTonya Taylor
Randall Tibbs
Ruth Jones
Michael Curley, Ph. D.
E. K. Williams, Ph. D.
Thomas Taylor, Ph. D.
Philippia Simmons
Iulia Muntele Ph. D. (2003)

References

1. W. Ensinger and G. K. Wolf, *Mat. Sci. and Eng.*, **A116** (1989) 1.
2. Y. Baba and T.A. Sasaki, *Mat. Sci. Eng.* **A115** (1989) 203.
3. C. G. Fountzoulas, J. D. Demaree, W. E. Kosik, W. Franzen, W. Croft and J. K. Hirvonen, *i-C₄Si₃O₂H_W Films Formed by Ion Beam Assisted Deposition*, *Mat. Res. Soc. Symp. Proc.* **279** (1993) 645-650.
4. W. Franzen, T. Tetreault, W. Kosik, W. Croft and J. K. Hirvonen, *Ion and Electron Beam Processing of Condensed Solids to Form Thin Films*, *Mat. Res. Soc. Symp. Proc.* **279** (1993) 825.
5. R. A. Kant and B. D. Sartwell, *Journal of Vacuum Science and Technology A8* (1990) 861.
6. W. Enzinger, A. Schroer and G.K. Wolf, *Surface and Coatings Tech.* **51** (1992) 21.
7. J. K. Hirvonen, T. G. Tetreault, G. Parker, P. Revesz, D. Land, J. Price, D. Simons and S. Stern, *Preparation and Characterization of Ion Beam Assisted Aluminum Oxide Films*, in *Beam Solid Interactions: Physical Phenomena*, edited by J. A. Knapp, P. Boresen and R. A. Zuhr (*Mat. Res. Soc. Symp. Proc.* **157**, Pittsburgh, PA, (1990) 13).
8. R. L. Zimmerman, D. Ila and C. C. Smith, *Resonant scattering assisted light element analysis*, *Nuclear Instruments and Methods in Physics Research B85* (1994) 68.

9. D. Ila, G. M. Jenkins, L. R. Holland, J. Thompson, L. Evelyn, A. Hodges, R. L. Zimmerman and I. Dalins, *Measurement of accumulated contaminants in glassy carbon by RBS, ERD and NRA*, **Nuclear Instruments and Methods in Physics Research B64** (1992) 439.
10. D. Ila, G. M. Jenkins, L. R. Holland, L. Evelyn and H. Jena, *A study of the thermally induced carbonization of phenolformaldehyde by combined ion beam and surface specific analyses*, **Vacuum 45**, No. 4 (1994) 451.
11. A. L. Evelyn, D. Ila, G. M. Jenkins, *RBS and Raman spectroscopy study of heat-treatment effect on phenolformaldehyde resin*, **Nuclear Instruments and Methods in Physics Research B85** (1994) 861.
12. T. Taylor, D. Ila, J. C. Cochrane, *RBS, AES, EDX and ESCA investigation of heat treatment effects on stainless steel alloy 440C*, **Nuclear Instruments and Methods in Physics Research B85** (1994) 904.
13. G. M. Jenkins, D. Ila, and E. K. Williams, *Oxygen Bombardment Induced Activation of Glassy Carbon*, **Materials Research Society Symposium Proceedings 304** (1993) 173.
14. D. Ila, A. L. Evelyn, and G. M. Jenkins, *Ion beam induced graphitization of phenolformaldehyde*, **Materials Research Society Symposium Proceedings 321**, (1994) 441.
15. D. Ila, R. L. Zimmerman and G. M. Jenkins, *Controlled Formation of Buried Layers of Carbon*, **Materials Research Society Symposium Proceedings 349** (1994)
16. A. L. Evelyn, D. Ila, R. L. Zimmerman and K. Bhat, D. B. Poker and D. K. Hensley, *"Effects of MeV ions on Pe and PVDC,"* **Nuclear Instruments and Methods in Physics Research B141**, 164-168 (1998)
17. R. L. Zimmerman, D. Ila, E. K. Williams, D. B. Poker, D. K. Hensley, C. Klatt and S. Kalbitzer, *"Ion Beam Synthesis of Au and Cu Nanoclusters in MgO"*, *Ion Beam Modification of Materials*, Amsterdam, 31-5 September 1998, **Nuclear Instruments and Methods in Physics Research B148**, 1064-1068 (1999)
18. T. Taylor, D. Ila, R. L. Zimmerman, J. C. Cochrane, P. R. Ashley, D. B. Poker and D. K. Hensley, *"Temperature Effects on the Fabrication of Optical Channels in Planar GaAs/AlGaAs Waveguides Using MeV Ions,"* **Nuclear Instruments and Methods in Physics Research B141**, 704-708 (1998)
19. D. Ila, R. L. Zimmerman, E. K. Williams, C. C. Smith, S. Sarkisov, D. B. Poker and D. K. Hensley, *"Ion Beam Induced Change in the Optical Properties of Photorefractive Materials,"* **Ion Beam Modification of Materials**, Amsterdam, 31-5 September 1998
20. A. L. Evelyn, D. Ila, R. L. Zimmerman, K. Bhat, D. B. Poker, D. K. Hensley, C. Klatt, S. Kalbitzer, N. Just and C. Drevet, *"Ion Beam Modification of PES, PS and PVC Polymers"* *Ion Beam Modification of Materials*, Amsterdam, 31-5 September 1998, **Nuclear Inst. and Methods in Physics Research B148**, 1141-1145 (1999)
21. R. L. Zimmerman, D. Ila, E. K. Williams, B. Gasic, A. Elsamadicy, A. L. Evelyn, D. B. Poker, D. K. Hensley and David J. Larkin, *"Gold, Silver and Copper Nanocrystal Formation in SiC by MeV Implantation,"* **Nuclear Instruments and Methods B** 166-167 (2000) 892-896,
22. D. Ila, E. K. Williams, R. L. Zimmerman, D. B. Poker and D. K. Hensley, *"Radiation Induced Nucleation of Nanoparticles in Silica",* **Nuclear Instruments and Methods B166-167** (2000) 845-850,
23. L. Evelyn, D. Ila, M. G. Rodrigues, R. L. Zimmerman, D. B. Poker and D. H. Hensley, *'RADIATION ENHANCED POROSITY AND ROUGHNESS OF BIOMATERIALS,'* **Materials Research Society Symposium FF Symposium Proceedings**, Boston 1999
24. C. I. Montele, D. Ila, E. K. Williams, D. B. Poker, D. K. Hensley, David J. Larkin and Iulia Montele, *"Fabrication of SiC Hydrogen Sensor by Pd Implantation",* **Materials Science Forum V** (2000) 338-1446
25. R. L. Zimmerman, D. Ila and J. Hirvonen, *"Optimized System for Hydrogen Detection,"* **Nuclear Instruments and Methods B118** (1996) 206-208.
26. C. I. Muntele, D. Ila and R. L. Zimmerman, *"Enhanced Hydrogen Detection and Depth Profiling System using Coincidence Techniques,"* *Invited paper at Denton accelerator conference, November 2000*